

GRAFT COPOLYMERIZATION OF ACRYLAMIDE ONTO POLY(N-PARA-TOLYLACRYLAMIDE) FILMS INITIATED BY CERIC ION

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ABSTRACT

Functional monomers having phenylcarbamoyl and p-tolylcarbamoyl were synthesized. Binary initiation system consisted of Ce^{4+} and these functional monomers could initiate acrylamide polymerization. It was found that acrylamide could graft copolymerize onto macromolecules having these functional monomers units. The formation of graft copolymer has been verified by its percentage of water absorption, contact angle with water, XPS and SEM photographs. The reaction mechanism was proposed and the main reactive site of graft copolymerization initiated by Ce^{4+} would take place predominantly at the functional pendant group.

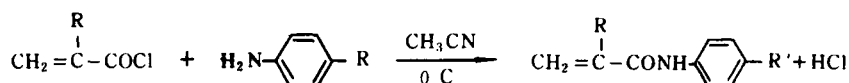
INTRODUCTION

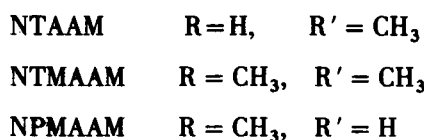
Graft copolymerizations of vinyl monomers onto natural and synthetic polymers by ceric ion have been reviewed by several authors^[1-5], and some articles concerned with the graft copolymerization of polyamide by ceric ion^[6,7]. Feng et al.^[8], have reported previously that ceric ion coupled with anilide could initiate acrylamide(AAM) polymerization. In this paper, functional monomers having phenyl and para-tolylcarbamoyl groups such as N-para-tolyl-2-methylacrylamide (NTMAAM), N-para-tolyl-acrylamide(NTAAM), and N-phenyl-2-methylacrylamide(NPMAAM) were synthesized, and the polymerization rate of AAM initiated by binary systems consisted of ceric ion and these functional monomers were determined, PNTAAM, PNTMAAM PNPMAAM and copolymers 1-6 were prepared by the copolymerization of functional monomer with methyl acrylate(MA) and methyl methacrylate (MMA) respectively. The graft copolymerization of AAM onto polymeric films with ceric ion, the effects of components of films and reaction condition on the copolymerization were investigated. The formation of graft copolymer was verified.

EXPERIMENTAL

Materials

Functional monomers: NTAAM, NTMAAM and NPMAAM functional monomers were synthesized from the reactions of acryloyl chloride or 2-methyl-acryloyl chloride with para-toluidine or aniline respectively at 0°C in acetonitrile solvent as described in the literature^[9].





The data of melting point and elementary analysis of these functional monomers were compiled in Table 1.

Table 1 Melting points and elementary analysis of functional monomers

Functional monomer	Melting point °C	Elementary analysis			
		C(%)	H(%)	N(%)	
NTAAM	141—142 (141)*	74.53	6.83	8.70	Calcd.
		74.59	6.76	8.63	Found
NTMAAM	88 (88—88.5)**	75.43	7.43	8.00	Calcd.
		75.89	7.61	7.98	Found
NPMAAM	85—85.5 (85—85.5)**	74.53	6.83	8.70	Calcd.
		74.23	6.99	8.68	Found

* From reference[9]

** From reference[10]

Reagents: AAM, MA, MMA monomers were chemical reagents and were purified by usual methods. Acryloyl chloride and 2-methylacryloyl chloride were prepared from the reactions of corresponding acids with benzoyl chloride respectively. The other chemical reagents such as ceric ammonium nitrate (CAN), dibenzoyl peroxide(BPO), 2,2'-azo-bis-isobutyronitrile(AIBN) and organic solvents such as N,N-dimethylformamide(DMF), formamide, methanol, acetone, ether were used directly.

Synthesis of polymers and film casting

Polymers and copolymers: 2 g of functional monomer, AIBN or BPO (0.3 mol % based on monomer), 4 mL DMF were mixed, then it was poured into a polymerization tube. After the oxygen in the tube was removed by nitrogen gas, the tube was sealed and the polymerization was carried out at 70°C for 10—20 hours. The polymer was precipitated from the ether or CH₃OH—H₂O mixed solution. The purified polymer was dissolved in DMF, and the intrinsic viscosity[η] was determined at 25 °C. Copolymers of functional monomer and MA or MMA were synthesized in the similar process.

Film casting: Homopolymer or copolymer was dissolved in acetone or DMF and then poured into a mould. After the solvent was evaporated, a transparent film was obtained with a thickness of 0.3—0.5 mm.

Graft copolymerization and characterization of grafted copolymers

Graft copolymerization: A piece of dried and weighed polymeric film was put into an AAM(2

mol/L) aqueous solution, which was then deaerated with nitrogen gas. CAN initiator was added and the reaction maintained at 40 or 50°C for 50–60 min with stirring and bubbling nitrogen gas through the reaction mixture. The concentration of the CAN initiator was selected in the range of $5\text{--}10 \times 10^{-3}$ mol/L. In order to remove the homopolymer PAAM and the remaining monomer, the grafted film was immersed in a formamide solvent and then washed with distilled water several times. The grafting percentage was calculated according to the following equation

$$G(\text{grafting}) \% = \frac{W - W_0}{W_0} \times 100$$

W is the weight of film after graft copolymerization and W_0 is the weight of film before the reaction.

Characterization of grafted copolymer:

1) Water absorption: The water absorption of film was determined according to the procedure described in the previous paper^[11].

2) Contact angle with water: The value of contact angle with water was determined by a JY-82 contact angle determination instrument.

3) Surface morphology and surface composition of film: The surface morphology of grafted film was observed with a scanning electron microscopy (SEM). The surface composition of film was calculated from the X-ray photoelectron spectrometry (XPS) measurement. The XPS spectra were obtained on a VG-ESCA LAB-5 electron spectrometer by using Al K α radiation under 10^{-9} torr vacuum. The anodic voltage was set at 12KV, irradiation current 20 mA was used for all the runs.

RESULTS AND DISCUSSION

1. Graft copolymerization of homopolymers having para-tolylcarbamoyl and phenylcarbamoyl pendant groups

It was found that binary systems consisted of ceric ion and NTAAM, NTMAAM, NPMAAM functional monomers could initiate AAM to polymerize in aqueous solution, and the polymerization rate R_p of these three functional monomers is as the following descending order^[12]

$$\text{NTAAM} > \text{NTMAAM} > \text{NPMAAM}$$

$R_p \times 10^4 \text{ (mol/L} \cdot \text{s)}$	15.2	10.7	3.98
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Table 2 shows the graft copolymerization of AAM onto the films of homopolymers of functional monomers. It can be seen that the grafting percentage is dependent on the reactivity of the functional monomer, the order of grafting activity is

$$\text{PNTAAM} > \text{PNTMAAM} > \text{PNPMAAM}$$

Obviously, the para-tolylcarbamoyl group has high promoting effect on the graft copolymerization of AAM initiated by ceric ion. An electron donating group, i. e. methyl group, on the benzene ring could increase the electron density on the carbonyl group, which would favor the coordination with ceric ion and enhance the rate of grafting reaction. While the functional monomer having α -methyl group, i.e. PNTMAAM, PNPMAAM, the steric hindrance effect would interfere the coordinating with ceric ion and retard the grafting reaction. The grafted films exhibit higher water absorption percentage and there were salient micrographs showing the grafts of the macrochain on the surface of the film, which can be observed from the SEM photographs as shown in Fig. 2—Fig.5.

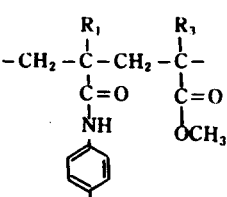
Table 2 Graft copolymerization onto polymeric film by ceric ion

Polymer	[η] (dl/g) (25°C, DMF)	Film weight (mg)	Grafting (%)	Water absorption(%)	
				Grafted film	Substrate
PNTAAM	0.716	28.4	168	219	3.4
PNTMAAM	0.393	40.5	20.5	52.3	2.2
PNPMAAM	0.446	36.0		6.2	5.0

[AAM] = 2 mol/L, [CAN] = 1×10^{-2} mol/L, 50°C, 50 min

2. Graft copolymerization of copolymers having para-tolylcarbamoyl or phenylcarbamoyl pendant groups

Copolymers 1—6 were synthesized from copolymerization of NTAAM, NTMAAM, NPMAAM and MA, MMA respectively

	Copolymer		R ₁	R ₂	R ₃	
	1	2	3	4	5	6
	poly(NTAAM-co-MA)	poly(NTAAM-co-MMA)	poly(NTMAAM-co-MA)	poly(NTMAAM-co-MMA)	poly(NPMAAM-co-MA)	poly(NPMAAM-co-MMA)
	H	H	CH ₃	CH ₃	CH ₃	CH ₃
	CH ₃	CH ₃	CH ₃	CH ₃	H	H
	H	H	H	H	CH ₃	CH ₃

Since graft copolymerization of AAM onto MA, MMA homopolymer or MA-MMA copolymer can not be initiated by ceric ion, the functional monomer units in copolymers will have predominant effect on the activity of graft copolymerization. When MA is the comonomer, the composition ratio

Table 3 Graft copolymerization onto copolymeric film by ceric ion

Copolymer (70/30)*	[η] (dl/g) (25°C, DMF)	Film weight (mg)	Grafting (%)	Water absorption (%)	
				Grafted film	Substrate
1 ^a	0.73	51.2	49.4	128	5.0
3 ^b	0.491	67.0	39.4	131	2.2
5 ^c	0.356	17.6	19.9		3.3
2 ^c	1.39	34.6	195	247	3.7
4 ^c	0.387	45.6	41.0	103	3.0
6 ^c	0.551	34.0		12.5	4.9

a [AAM] = 2.0 mol/L, [CAN] = 5×10^{-3} mol/L, 45°C, 50 min

b [AAM] = 2.0 mol/L, [CAN] = 10×10^{-3} mol/L, 50°C, 55 min

c [AAM] = 2.0 mol/L, [CAN] = 10×10^{-3} mol/L, 50°C, 60 min

* Molar feed of functional monomer to MA or MMA in copolymerization

of the molar feed of functional monomer to MA of the copolymeric film is 70/30, the results for graft copolymerization obtained is shown in Table 3.

Obviously, copolymer having the more reactive functional monomer has higher grafting percentage, and the following order is observed.



When MMA is used as a comonomer the similar results are obtained as shown in Table 3. The order of grafting percentage is as follows:



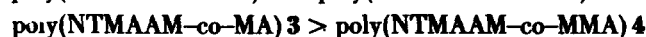
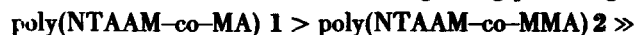
Table 4 Graft copolymerization of AAM onto copolymeric films

Copolymer (80/20)*	[η] (dl/g) (25°C, DMF)	Film weight (mg)	Grafting (%)	Water absorption (%)	
				Grafted film	Substrate
1	0.563	34.3	334	177	3.1
2	0.817	37.3	312	158	3.6
3	0.366	62.3	17.5	85.4	0.3
4	0.441	25.2	15.5	65.2	1.9

[AAM] = 2.0 mol/L, [CAN] = 10×10^{-3} mol/L, 50°C, 60 min

* Molar feed of functional monomer to MA or MMA in copolymerization

Table 4 shows that the order of grafting percentage is as follows:



This result shows that the structural effect of functional monomer unit is more obvious than that of comonomer unit in copolymer 1—4. Therefore, the values of grafting percentage of 1 and 2 are much greater than that of 3 and 4, while the difference between 1 and 2 or 3 and 4 is slightly.

Table 5 Graft copolymerization of AAM onto copolymeric films

Copolymer (90/10)*	[η] (dl/g) (25°C, DMF)	Film weight (mg)	Grafting (%)	Water absorption	
				Grafted film	Substrate
1	0.678	63.2	215	320	5.0
2	0.680	56.8	201	269	5.7
4	0.461	40.4	40.8	178	0.3
5	0.467	69.5	2.3	20.7	4.7
6	0.446	21.4	0.9	12.0	3.6

[AAM] = 2.0 mol/L, [CAN] = 10×10^{-3} mol/L, 50°C, 60 min

* Molar feed of functional monomer to MA or MMA in copolymerization

Obviously, copolymer 6 consists of the less active functional monomer NPMAAM and having a steric hindrance effect comonomer MMA will exhibit very small activity on grafting reaction and the grafting percentage is observed as the following order (see Table 5)

$$1 > 2 \gg 4 \gg 5 > 6$$

Other factors effect on graft copolymerization

1) Effect of composition of film When the composition of feed monomer of functional monomer to MMA was below 60/40, it could not be initiated by ceric ion to copolymerize. Increasing the composition of functional monomer would favour the grafting reaction. When the concentrations of CAN and AAM were fixed at 5×10^{-3} and 2.0 mol/L at temperature 45°C, 60 minutes, the grafting percentage(G %) increased with the increasing of the functional monomer composition of copolymer 1. The following results were obtained. G%: 9.1(NTAAM/MA = 70/30); 32.0 (80/20); 71.5(90/10).

2) Effects of reaction condition When the reaction was carried out at 30—40°C the graft copolymerization did not take place, while at 55—60°C the hydrolysis reaction of the paratolylcarbonyl would occur. Therefore, the graft copolymerization was favoured to perform at 45—50°C. The concentration of ceric ion also would influence the grafting reaction. When a copolymeric film with composition 70/30 was used for graft copolymerization, the concentration of CAN was 1×10^{-3} mol/L no graft copolymerization was observed, but it was easy to take place when [CAN] = 5— 10×10^{-3} mol/L and the grafting percentage was 12—30%. With further increase of concentration of CAN, the grafting percentage would turn down at [CAN] = 30×10^{-3} mol/L. This may be due to the competition reaction of homopolymerization of AAM.

3. Characterization of graft copolymer

Water absorption and contact angle The water absorption of grafted film was always greater than that of original one (substrate), as shown in Table 2—5. This was due to the contribution of the grafting PAAM macromolecular chain, which had a higher water-absorbing. With the increase of hydrophilic of grafted film the value of contact angle(θ) with water decreased, as shown in Table 6.

Table 6 Change on the values of contact angle with water

Copolymeric film	Monomer feed (molar ratio)	θ of substrate (°)	θ of grafted film (°)	grafting (%)
2	70/30	91.2	59.3	115
3	70/30	96.2	77.9	36.2
3	90/10	91.3	85.9	17.9
4	60/40	89.0	76.3	14.6
4	70/30	91.0	77.3	8.9
6	60/40	91.0	86.3	7.6

SEM photographs When the SEM photographs of the grafted films were compared with that of original one, it was found that in the former case there were salient micrographs, showing the grafts of the macromolecular chain on the surface of film, but it was not observed in the latter case, as shown in Fig. 1—5.



Fig. 1 SEM photograph of PNTAAM ($\times 463$)

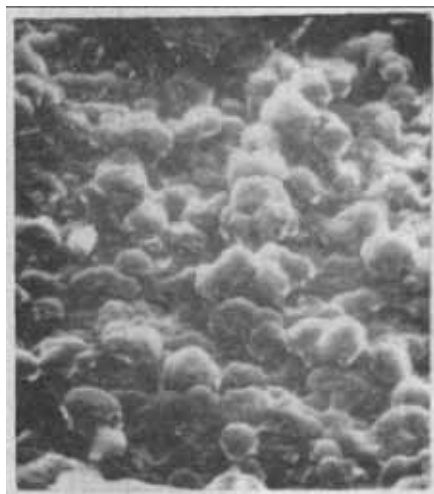


Fig. 2 SEM photograph of poly(NTAAM-gAAM ($\times 218$)
G: 54%



Fig. 3 SEM photograph of poly(NTMAAM-g-AAM)
($\times 418$) G: 20.5%

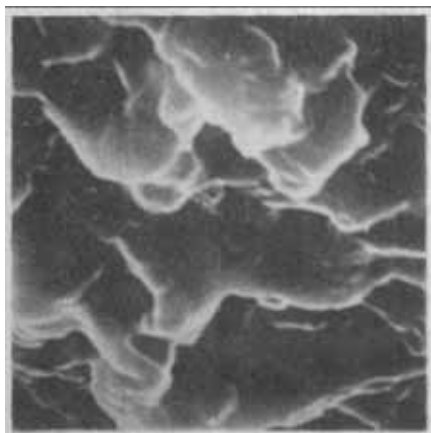


Fig. 4 SEM photograph of
poly[(NTAAM-co-MA)-g-AAM] ($\times 2340$), G: 29.3%

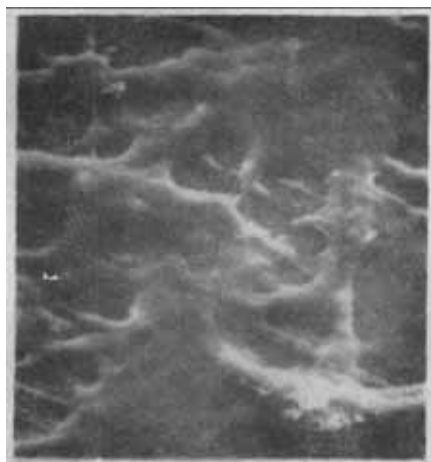


Fig. 5 SEM photograph of poly[(NTAAM-co-MMA)-g-AAM]
($\times 230$), G: 3.7%

XPS spectra The surface composition of the film was measured by XPS spectra. Since the grafting of PAAM would increase the content of O and N, the ratio of C/N and C/O on the surface of grafted film were smaller than that of the original one. The data were compiled in Table 7.

Table 7 Values of C/N and C/O by XPS

Copolymeric film	Monomer feed (molar ratio)	Before graft		After graft		Grafting (%)
		C/N	C/O	C/N	C/O	
Poly(NTAAM-co-MMA)	70/30	16.5	5.92	5.46	4.07	115
Poly(NTMAAM-co-MA)	60/40	33.8	6.02	10.1	3.92	7.4
Poly(NTMAAM-co-MMA)	70/30	22.2	6.80	4.78	3.57	12.0

Fig. 6 showed the XPS spectrum of grafted film. There were two C_{1s} peaks for carbon core electron. The major C_{1s} peak had binding energy of 286.5 eV and a small peak of 289 eV. The latter peak was due to the contribution of amido linkage. While only the major C_{1s} peak had binding energy of 285.5 eV was observed in the spectrum of the original one, as shown in Fig. 7.

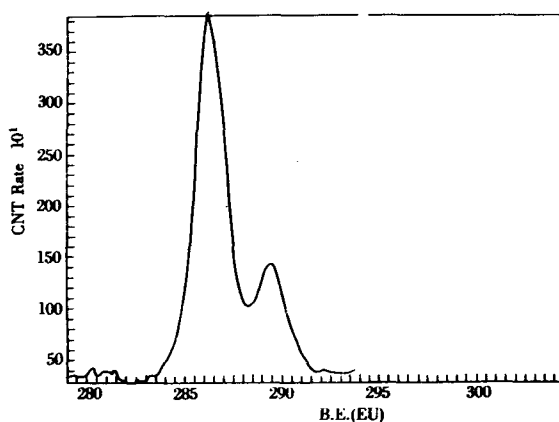


Fig. 6 XPS spectrum of grafted film

Poly[(NTAAM-co-MMA)-g-AAM] (NTAAM/MMA = 70/30)

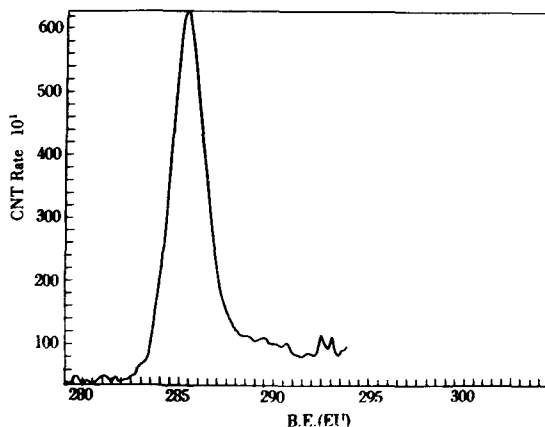


Fig. 7 XPS spectrum of original film

Poly(NTAAM-co-MMA) (NTAAM/MMA = 70/30)

From the results mentioned above, AAM initiated by ceric ion would easily be grafted onto the film of macromolecules having para-tolylcarbonyl group. The grafted copolymer has been verified by SEM, XPS, the grafting reaction takes place predominately at the functional monomer unit with the grafting site at the N-H of the amido linkage as proposed in the previous paper^[8] on the studies of the initiation mechanism of ceric ion and anilide systems.

Keywords

Acrylamide, Functional monomers, N-para-tolylacrylamide, Copolymers, Graft copolymerization initiated by ceric ion, Characterization of grafted copolymers by SEM, XPS.

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